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Evidence for an unconventional superconducting order parameter in $YBa_2Cu_3O_{6.9}$

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We report measurements of the dynamic resistance R_D of a dc SQUID formed by two contacts between two different edges of a single crystal of $YBa_2Cu_3O_{6.9}$ and a Nb block. The phase of the field-induced R_D oscillations was compared with those of two adjacent SQUID's, each formed by two Nb-Nb contacts. We find a phase difference of $160\pm30°$ between the oscillations of the composite SQUID and those of the SQUID's formed by Nb-Nb junctions. A possible explanation for this reproducible effect is that this cuprate superconductor has an unconventional order parameter.

A fundamental unsolved problem in superconductivity is to establish the symmetry of the superconducting order parameter of the high-T_c cuprate superconductors. Conventional BCS theory with phonon-mediated coupling favors an order parameter with s-wave symmetry, as is believed to be the case for common superconductors. Based on various experiments and different model calculations it has been suggested that an order parameter with d-wave or $(s+id)$ symmetry may be more appropriate to describe the symmetry of the superconducting state of the cuprate materials. The relevant facts and ideas are summarized in Ref. 1. Soon after the discovery of the cuprate superconductors it was suggested that their electronic properties might be described by the Hubbard model near half filling.[2] With this assumption, Bickers and co-workers,[3] and also Kotliar[4] proposed that an exchange of antiferromagnetic spin fluctuations in a half-filled two-dimensional (2D) Hubbard model could provide a pairing mechanism leading to a $d_{x^2-y^2}$ symmetry state. Experimental results supporting both s- and d-wave-type order parameters are more recent. Measurements of the penetration depth and its temperature dependence $\lambda(T)$ which suggest an s-wave symmetry are described in Ref. 5 and later Ref. 6. A review of various experimental results concerning $\lambda(T)$ was given by Beasley.[7] Further experimental results for $\lambda(T)$, discussed in Ref. 8, however, were interpreted as evidence for d-wave symmetry. Measurements of NMR relaxation rates,[9] and their corresponding phenomenological interpretations[10,11] have also suggested a possible d-wave symmetry of the order parameter for $YBa_2Cu_3O_{6.9}$. Meanwhile a theoretical basis for an anisotropic s-wave order parameter was developed by Chakravarty and co-workers[12] claiming to provide a consistent explanation of all the above measurements.

The only experiments that can really distinguish an anisotropic s-wave from a d-wave state are those which are sensitive to the phase of the order parameter. For that purpose, measurements sensitive to tunneling of paired charge carriers seem most promising, and experiments based on Josephson tunneling or SQUID performances probing phase coherence were devised. A recent experiment by Wollman and co-workers[13] that analyzed the phase of single-crystal $YBa_2Cu_3O_{6.9}$ (YBCO)-Pb SQUID's suggested d-wave symmetry. However, a more recent tunneling experiment by Chaudhari and Lin[14] using thin epitaxial films of YBCO with grain-boundary Josephson junctions suggests s-wave symmetry. This type of experiment was initially inspired by theoretical results of Geshkenbein and Larkin[15] and later work by Sigrist and Rice.[16] Following similar ideas we attempted to compare the response of a dc SQUID formed by two junctions between a high-T_c (YBCO) and a conventional (Nb) superconductor with that of SQUID's fabricated from Nb alone. Our experimental results imply that the symmetry of the superconducting order parameter of $YBa_2Cu_3O_{6.9}$ is not of a simple s-wave variety.

The construction of the SQUID's is shown schematically in Fig. 1. The hybrid $YBa_2Cu_3O_{6.9}$ (YBCO)-Nb SQUID consisted of a YBCO crystal of size $1.0\times0.5\times0.25$ mm pressed into a 0.5 mm wide slot in a Nb half-cylinder that

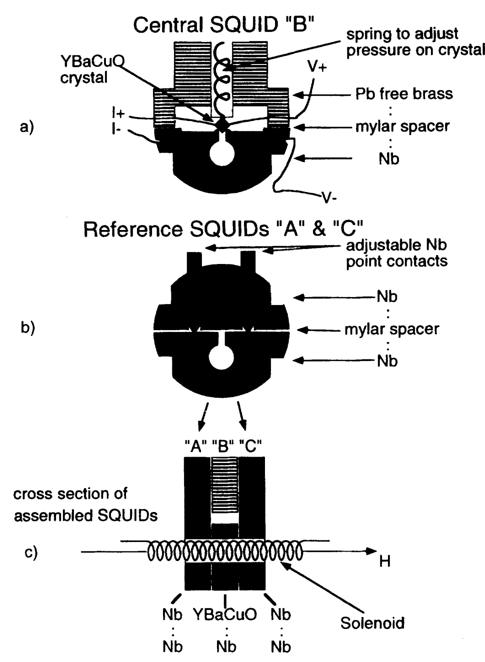

FIG. 1. Schematic diagrams of the SQUID's that were constructed (a) and (b), and a schematic sketch of the complete setup (c). The two reference Nb-Nb SQUID's were placed on either side of the $YBa_2Cu_3O_{6.9}$-Nb SQUID in order to ascertain the same flux configuration. A solenoid was placed through all three SQUID's to provide the excitation flux of magnitude $\Phi_0/2$.

FIG. 2. A photograph of the twin-free $YBa_2Cu_3O_{6.9}$ crystal wedged into the Nb slot. In the upper half, part of the SQUID loop may be seen. The contact pressure between the crystal and the Nb block could be adjusted from the top of the cryostat.

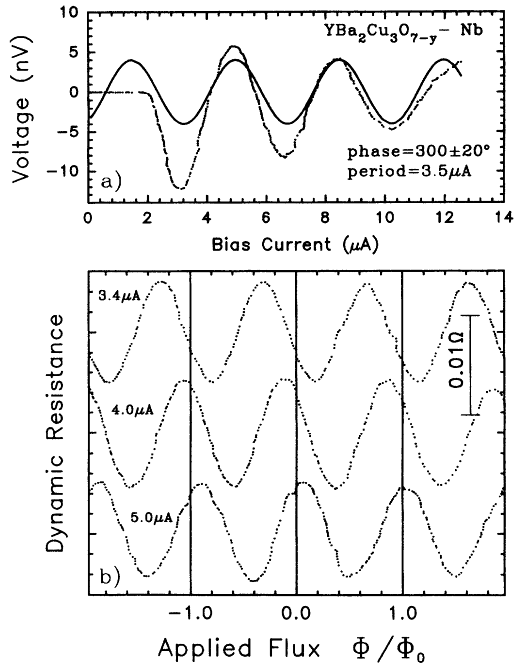

FIG. 3. (a) Hybrid SQUID output voltage at zero applied dc flux vs bias current. The solid line is a sinusoidal approximation fitting to the phase and the period. (b) Dynamic resistance of the hybrid SQUID as a function of externally applied flux and different bias-current values. The curves have been shifted vertically for clarity. All data were taken at 4.2 K.

has a 2.0 mm diameter flux cavity in the center. The platelike single crystal used was grown by the slow-cooling method.[17] It was chosen for its smooth edges and perpendicular corners, which was apparent down to the submicron level by later examination with an electron-beam microscope. The crystal was inserted so that one Josephson junction would inject current into the *a* direction, and the other into the *b* direction. A photograph of the mounted crystal is shown in Fig. 2. Since the directionality of injection of the electrons is important to obtain phase information from the order parameter, the junction was carefully prepared. A soft Nb burr was used to make contact to the $YBa_2Cu_3O_{6.9}$ crystal instead of a sharp needle. This was to prevent the Nb from boring into the crystal and causing electrons to be injected in all directions. The intrinsic insulating surface layer of the $YBa_2Cu_3O_{6.9}$ and a heavily oxidized Nb piece ensured that an superconductor-insulator-superconductor (SIS) tunnel junction with a low critical current ($I_c < 10$ μA) was produced. The current and voltage leads were attached directly to the $YBa_2Cu_3O_{6.9}$ crystal and the Nb block with silver epoxy and paint, respectively. The crystal was embedded in Stycast 1266 epoxy for mechanical support and attached to a spring-loaded mount. The pressure on the crystal was controlled from the top of the Dewar until point contacts for suitable SQUID performance were obtained. The pressure was sufficient to leave small indentations in the Nb, but the $YBa_2Cu_3O_{6.9}$ was not visibly affected. The indentations give an upper bound of the size of the junction's area to be 12×10^{-10} m^2. Two reference SQUID's were placed on either side of the hybrid SQUID as shown in Fig. 1(c). The Nb-Nb SQUID's [Fig. 1(b)] are similar to those constructed by Zimmerman and Silver.[18] They consist of two Nb semidisks, separated by a Mylar film and clamped together. The Josephson junctions were achieved with pointed Nb screws that punctured the Mylar. Their position, and thus the critical currents of the junctions, was controlled from the top of the cryostat. All the SQUID's were shunted with a 1 Ω strip to eliminate hysteresis, so their current vs voltage *IV* curves exhibited resistively shunted junction behavior. The SQUID's were designed to have similar characteristics to facilitate a comparison of their phases. The critical currents ranged from 1 to 5 μA, and for small critical currents, noise rounding occurred which allowed for SQUID oscillations to occur at bias currents below the critical current. A typical value for β was 30 which means that the critical-current amplitude modulation was approximately 3%. The inductance of the SQUID's was 2.9 nH and the dynamic resistance (R_D) was approximately 10 mΩ. This leads to the prediction that the SQUID oscillations should be approximately 4 nV, which was observed.

A small 40 turn solenoid was inserted through the cavities of the SQUID's as shown in Fig. 1(c). It carried a 720 Hz ac current (0.22 μA p.-p.) corresponding to a field amplitude of $\Phi_0/2$. A lock-in amplifier used this 720 Hz signal as a reference to measure the voltage from the preamplifier. The SQUID voltage was amplified first with a 10:1000 PAR 125 low-noise transformer to increase the impedance by 10^4, and a battery-powered Burr-Brown INA 110 differential amplifier with gain 100. This amplification technique is similar to that described by Clarke.[19] The performance of our hybrid SQUID is shown in Fig. 3. In Fig. 3(a), the SQUID voltage, proportional to the dynamic resistance R_D, is plotted versus bias current I_B for zero average field. The same type of signals now obtained for different constant bias currents, as a function of external dc magnetic field are shown in Fig. 3(b).

It is the phase of these oscillations which provides the essential information sought in this experiment. Assuming a d-wave-type order parameter as a promising candidate for cuprate superconductors, it is expected that the most likely order parameter has $d_{x^2-y^2}$ symmetry resulting in four perpendicular lobes in a k-space plane and a phase difference of π between adjacent lobes. With our experimental configuration we would track this phase difference by a corresponding phase shift of voltage oscillations of our hybrid SQUID with respect to those of the conventional, all-Nb devices.

The experiments were performed in an rf shielded room and the leads were filtered for frequencies above 10 kHz. A Pb superconducting cylinder with a cap surrounded the apparatus to shield against ambient magnetic-field variations. No attempt was made to shield the earth's field as the SQUID assembly is used to measure a relative phase shift. Even with μ-metal shielding the ambient field near the SQUID's would be of the order of many flux quanta because these SQUID's are periodic in a field of 2.8 μG.

When one SQUID is operating, the field generated by its own bias current will shift the phase of its neighbors. For this reason each SQUID was operated successively and not at the same time. The bias current may also affect the SQUID in operation, unless the junctions are perfectly balanced. If the current does not divide equally through each Josephson junction, a field causing a phase shift proportional to I_B is generated. The junction imbalance can be quantified with the parameter α defined by $I_L=(1-\alpha)I_B/2$, and $I_R=(1+\alpha)I_B/2$, where I_L and I_R are the currents through the left and right junction of the SQUID, respectively. The total current through the SQUID is $I_B=I_L+I_R$ and $J=I_R-I_L$ is the circulating current that causes the bias-current phase shifts displayed in Figs. 3 and 4. This effect is demonstrated in Fig. 3(b) for the YBCO-Nb SQUID. What needs to be evaluated is the phase for $I_B=0$ and zero applied dc flux because each SQUID has a different degree of imbalance. In Fig. 3(a) the YBCO-Nb SQUID voltage at zero applied dc flux vs I_B is shown. In order to extract the phase of the SQUID at zero bias current a sine wave with amplitude 4 nV is superimposed on the diagram chosen to fit the phase and period. No attempt is made to fit to the amplitude of the oscillations.

Since the additional flux through the SQUID is just $\Phi=JL$, the imbalance can be related to the bias-current period, ΔI_B, by $\alpha=\Phi_0/L\Delta I_B$. This yields $\alpha\sim0.25$ for all the SQUID data shown in Fig. 4. Figure 4 shows the induced R_D oscillations and their extrapolation to $I_B=0$ for all three SQUID's. First, they were all adjusted to have low critical currents, and then the bias-current scans were successively taken for all three. The same amplification device was used for all SQUID's to ensure that any difference in phase originates from the SQUID's themselves. As indicated on the plot, the two outer Nb-Nb SQUID's measured the same flux with a phase of 80°, while the YBCO-Nb SQUID consistently measured a phase of 240°, giving a relative phase shift of 160°. The uncertainty of the phase angles was estimated from the fits to be approximately ±20°. Since the two outer Nb-Nb SQUID's measure the same flux, at least modulo $\pm n\Phi_0$, one would expect the central SQUID to also contain the same flux. The same experiment with a different crystal but with only one Nb SQUID operating also consistently

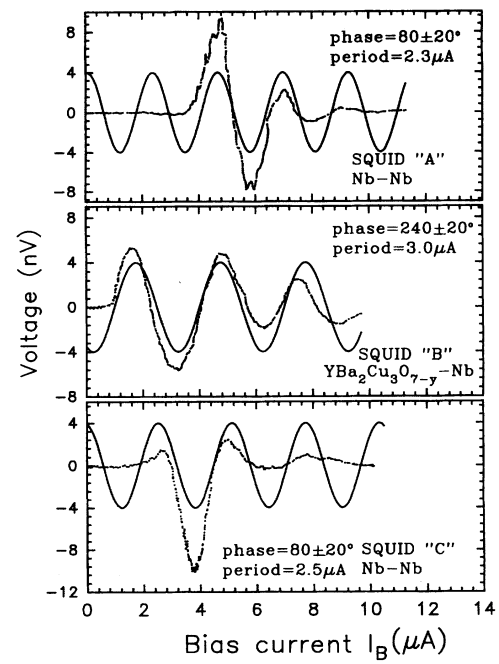

FIG. 4. Output voltages of all three SQUID's as a function of bias current. The fitting sine waves with the indicated phases, and period are shown as solid lines. Note that the phase on SQUID's "A" and "C" is the same, while the $YBa_2Cu_3O_{6.9}$-Nb SQUID differs by 160±30°.

resulted in a relative phase shift of 150±30°. Occasionally some flux will jump into the apparatus when the SQUID's are mechanically disturbed and this causes a different phase for all SQUID's. Upon reducing vibrations, SQUID's "A" and "B" had the same phase on all occasions and it was found that the YBCO-Nb SQUID "C" showed a relative phase shift of 160°.

All the curves presented here were stable from drift for periods on the order of 30 min. Beyond this time scale the phase may shift due to flux motion in the sample, and so all the measurements were taken within a few seconds, one after another. To ensure that the bias current does not introduce flux into the sample, I_B was increased to as high as 3 mA on one occasion. Upon reducing this current, the SQUID oscillations remained identical, indicating that there are no hysteretic effects due to bias current. This test should also eliminate the possibility of trapped flux within the junctions themselves. The Josephson penetration depth was $\lambda_J\sim11$ μm, which is of the order of the junction size, and which implies that there is only one vortex present in the junction at any time in low fields. A trapped vortex is expected to be dislodged by this test since the force on the vortex is proportional to the bias current. Since no hysteresis was ever observed we believe that no flux pinning within the junction is present. It is unlikely that flux motion in bulk $YBa_2Cu_3O_{6.9}$ or Nb due to bias currents should occur at $T=4.2$ K in the current and field regions of this experiment.

The crystal used in the run whose results are presented here was removed from the epoxy and examined for twins. Both scanning electron microscopy and polarized-light inspection revealed the absence of any twin or even microtwin boundaries in this specimen. Theoretically it is not known whether a superconducting order parameter will be locked along certain directions of the crystal structure. Since the crystal giving the results shown in Figs. 3 and 4 proved to be twin free, we do not speculate about the possible influence of twin boundaries at this point.

As we argued above, we may safely assume that the flux through the three SQUID's is the same modulo $\pm n\Phi_0$. We also believe that the particular orientation of the crystal in our hybrid SQUID setup is suitable to pick up phase differences within the superconducting order parameter. Hence it must be concluded that the $160\pm30°$ relative phase shift is due to an unconventional order parameter in superconducting $YBa_2Cu_3O_{6.9}$. The data currently cannot distinguish between pure d-wave symmetry expected to give a phase shift of 180°, and $(s+id)$ symmetry where any phase shift seems possible. It seems difficult to reconcile an electron-phonon attractive interaction with a superconducting state originating from d-wave pairing. Because of this an important implication of our experimental findings would be that superconductivity in this material most likely is triggered by other interactions.

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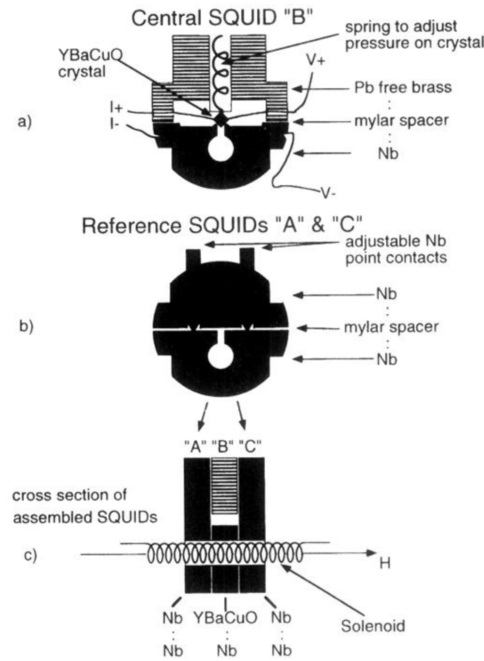

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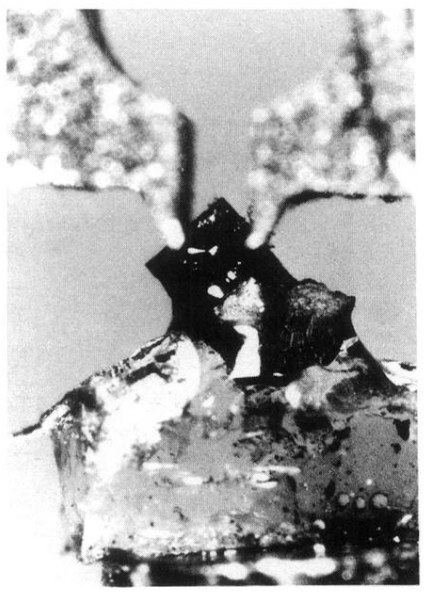

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